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Synthesis, properties and solution speciation of lanthanide chloride complexes of triphenylphosphine oxide

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Abstract

The reaction of Ph_3PO with $LnCl_3 \cdot nH_2O$ ($Ln = La–Lu \neq Pm$) in a 3.5:1 ratio in acetone produces $[LnCl_3(Ph_3PO)_3]$, whilst from a 6:1 ratio in ethanol the products are $[LnCl_2(Ph_3PO)_4]Cl \cdot n$(solvate). In the presence of $[NH_4][PF_6]$ in ethanol solution, $[LnCl_2(Ph_3PO)_4]PF_6$ can be isolated. The last complexes are stable in solution but the $[LnCl_3(Ph_3PO)_3]$ and $[LnCl_2(Ph_3PO)_4]Cl$ partially interconvert in non-coordinating solvents, the neutral species being preferred by the lighter lanthanides, the cationic tetrakis complexes becoming more favoured towards the end of the series. The complexes have been characterised in the solid state by analysis and IR spectroscopy and in solution by $^{31}P\{^1H\}$ NMR spectroscopy and conductance measurements. The crystal structures of *trans*-$[LnCl_2(Ph_3PO)_4]Cl \cdot nEtOH$ ($Ln = Tb$ or Yb) and *mer*-$[LnCl_3(Ph_3PO)_3] \cdot 0.5Me_2CO$ ($Ln = La$ or Ce) are reported and discussed.

Keywords: Lanthanides; Phosphine oxides; Crystal structures

1. Introduction

Phosphine oxides have often been chosen as suitable ligands for complexing the oxophilic lanthanide(3+) ions and have been used in solvent extraction separation processes [1]. The most thoroughly studied systems are the lanthanide nitrates with Ph_3PO, and Ph_2MePO where complexes of types $[Ln(NO_3)_3(R_3PO)_3]$ ($Ln = La–Lu$, $\neq Pm$), $[Ln(NO_3)_3(Ph_3PO)_4]$ ($Ln = La$, Ce, Pr, Nd) and $[Ln(NO_3)_2(R_3PO)_4]^+$, ($Ln = Tb–Lu$) have been characterised [2–6]. X-Ray crystallographic studies have shown that a range of 8-, 9-, and 10-coordinate structures are present [3–6]. Solution speciation in organic solvents (as established by $^{31}P\{^1H\}$ NMR and conductance studies) also varies along this series of complexes with $[Ln(NO_3)_3(R_3PO)_3]$ usually present for $Ln = La–Gd$, whilst for the later elements mixtures of $[Ln(NO_3)_3(R_3PO)_3]$ and $[Ln(NO_3)_2(R_3PO)_4]^+$ are observed.

For lanthanide chloride systems, the literature is based upon a few examples, is inconsistent and contains little data [1,7,8]. These reports indicate $[Ln(R_3PO)_xCl_3]$ ($x = 3$ or 4) often as solvates, can be isolated and are non-electrolytes in solution implying 6- and 7-coordinate lanthanide, respectively. In the presence of Lewis acids such as $FeCl_3$ or $CuCl_2$, $[LnCl(Ph_3PO)_5]^{2+}$ form [8]. Recent studies of the HMPA ($OP(NMe_2)_3$) complexes have established 6-coordinate $[LnCl_3(HMPA)_3]$ and crystal structures have been reported for *fac*-$[SmCl_3(HMPA)_3]$ and *mer*-$[LnCl_3(HMPA)_3]$ ($Ln = Yb$ or Dy) [9–11]. Recent detailed studies of the reactions of yttrium halides ($X = Cl$, Br or I) with Ph_3PO, Ph_2MePO and Me_3PO have revealed a range of complexes can be isolated depending upon the R_3PO and the reaction conditions used including $[YX_2(Ph_3PO)_4]^+$, $[YX_3(Ph_2MePO)_3]$, $[YCl(Ph_3PO)_5]^{2+}$, $[YCl_2(Ph_2MePO)_4]^+$, and $[Y(Me_3PO)_6]^{3+}$ [12]. We have also reported that Me_3PO, $LnCl_3 \cdot nH_2O$ and

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NH_4PF_6 react in methanol solution to produce octahedral $[Ln(Me_3PO)_6][PF_6]_3$ [13].

2. Results and discussion

Based upon analogies with the corresponding nitrates [3–6], the limited literature data on chloride systems [1,7] and preliminary experiments, we synthesised two series of complexes $[LnCl_3(Ph_3PO)_3]$ and $[LnCl_2(Ph_3PO)_4]PF_6$. The former were obtained in modest yield from reaction of $LnCl_3 \cdot nH_2O$ with 3.5 equivalents of Ph_3PO in acetone and the latter from reaction of $LnCl_3 \cdot nH_2O$ with Ph_3PO and NH_4PF_6 in a 1:4.5:1 molar ratio in absolute ethanol. Analytical and spectroscopic data showed that both series of complexes were prone to retain solvent and prolonged drying in high vacuum is necessary, although in some cases (vide infra) even then lattice solvent is retained. The $[LnCl_3(Ph_3PO)_3]$ complexes cannot be recrystallised from chlorocarbons or acetone unless some Ph_3PO is added, in its absence the products have markedly lower (and variable) C, H content and appear to be mixtures. Acetone or ethanol solutions of $[LnCl_3(Ph_3PO)_3]$ left to evaporate in the open laboratory hydrolyse with displacement of the Ph_3PO, and in the extreme, the products are Ph_3PO and hydrated lanthanide chlorides, one example of which $[Ce_2Cl_2(H_2O)_{14}]Cl_4$ was characterised by an X-ray study [14]. The reactions of $LnCl_3 \cdot nH_2O$ with Ph_3PO in absolute ethanol are less clear cut, it being possible to isolate $[LnCl_3(Ph_3PO)_3]$ and/or $[LnCl_2(Ph_3PO)_4]Cl \cdot n(\text{solv})$ depending on the Ln involved and the conditions. The $[LnCl_2(Ph_3PO)_4]Cl \cdot n(\text{solv})$ separate from ethanol solution containing a 6:1 molar ratio of $Ph_3PO:LnCl_3 \cdot nH_2O$. Although the analytical data (Table 1) are in reasonable agreement with formulae such as $[LnCl_2(Ph_3PO)_4]Cl \cdot 2H_2O$ or $[LnCl_2(Ph_3PO)_4]Cl \cdot 3EtOH$, ^1H NMR spectroscopy suggests that a mixture of water and ethanol is present which probably varies from sample to sample. The solvate water/ethanol is not removed in vacuo at room temperature and although it is lost on heating, this was generally avoided since it may be accompanied by some decomposition of the cations.

2.1. $[LnCl_2(Ph_3PO)_4]PF_6$

These were obtained as powders directly from the preparations, with analytical and IR data (weak features at ~3300 and 1650 cm^{-1}) suggesting that the first members of the series are hydrates (Table 1). The complexes are readily soluble in chlorocarbons, and poorly soluble in alcohols or acetone. The IR spectra show strong rather broad $\nu(PO)$ modes in the range 1139–1150 cm^{-1} which increase along the series La–Lu (Table 2) and which compare to 1195 cm^{-1} in Ph_3PO [12]. Weak features in the range 225–240 cm^{-1} are assigned as $\nu(Ln–Cl)$, and the ν_3 and ν_4 modes of $[PF_6]^-$ are observed at 844 and 560 cm^{-1} [15]. In 10^{-3} mol dm^{-3} CH_2Cl_2 solutions they have conductivities in the range 15–17 Ω^{-1} cm^2 mol^{-1} which are interpreted as 1:1 electrolytes [1] (the usual range for 1:1 electrolytes in this solvent is 20–25 Ω^{-1} cm^2 mol^{-1} [4,5,12], the lower values here being attributable to the very large ions). Addition of Ph_3PO to these solutions does not increase the conductance, showing that there is no tendency to displace further chlorides in this way. The ^1H NMR spectra are uninformative showing the expected phenyl protons, broadened and shifted in the paramagnetic complexes. The $^{31}P\{^1H\}$ NMR spectra (Table 2) show single resonances for the cations, in the cases of the paramagnetic Ln's broadened and shifted in generally similar ways to those reported for the nitrate systems [4,5], and qualitatively consistent with theoretical predictions [16]. Only $[GdCl_2(Ph_3PO)_4]PF_6$ fails to exhibit a resonance presumably due to fast relaxation by the gadolinium ion. For the elements Eu–Lu addition of Ph_3PO to the solutions results in a new resonance at δ 28 due to Ph_3PO and leaves the resonance of the cation unchanged showing exchange between free and coordinated phosphine oxides are slow on the NMR timescale. For Ce–Sm separate resonances for the cation and Ph_3PO are also observed but these are broad at 295 K indicating some slow exchange, and for $[LaCl_2(Ph_3PO)_4]PF_6$ only a single resonance is observed at 295 K which on cooling below 230 K splits showing exchange is fast at ambient temperatures. The observation of a single sharp $^{31}P\{^1H\}$ resonance for the diamagnetic La and Lu complexes indicates that all these cations are likely to be *trans* isomers, although the broadening caused by the lanthanide paramagnetism in most other cases is sufficient to prevent resolution of closely spaced resonances (in the diamagnetic Y complexes for example, phosphine oxides in geometrically different environments or in different complexes had $^{31}P\{^1H\}$ resonances which covered only a 1–2 ppm range [12]). Addition of anhydrous $[Bu_4N]Cl$ to solutions of $[LnCl_2(Ph_3PO)_4]^+$ in CH_2Cl_2 resulted in new resonances identified as free Ph_3PO and $[LnCl_3(Ph_3PO)_3]$ showing the expected equilibria are established, although for the later lanthanides, even with excess Cl^- the tetrakis cation is still the major species present. If "wet" $[Bu_4N]Cl$ was added to these solutions, some Ph_3PO was displaced but new $^{31}P\{^1H\}$ resonances were also generated which presumably result from water entering the coordination sphere of the lanthanide.

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[1] Although dichloromethane is not commonly used for conductance measurements, we have used it successfully for other series of phosphine oxide complexes. In the present case it was chosen to permit direct comparisons of the conductances with the NMR data obtained in this solvent. The lability and ease with which phosphine oxides are lost from these complexes makes the choice of solvent important.

Table 1
Analytical and physical data

Complex	%C [a]	%H	Λ (Ω^{-1} cm^2 mol^{-1} [b])	
			[c]	[d]
$[LaCl_3(Ph_3PO)_3]$	59.9(60.1)	4.4(4.5)	1	3
$[CeCl_3(Ph_3PO)_3]$	59.5(60.0)	4.4(4.2)	1	4
$[PrCl_3(Ph_3PO)_3]$	60.0(59.9)	4.2(4.2)	2	6
$[NdCl_3(Ph_3PO)_3]$	60.1(59.8)	4.0(4.2)	2	7
$[SmCl_3(Ph_3PO)_3]$	58.8(59.4)	4.2(4.2)	2	7
$[EuCl_3(Ph_3PO)_3]$	59.7(59.3)	4.3(4.2)	2	8
$[GdCl_3(Ph_3PO)_3]$	59.6(59.0)	4.0(4.1)	4	11
$[TbCl_3(Ph_3PO)_3]$	58.5(59.0)	4.3(4.1)	6	14
$[DyCl_3(Ph_3PO)_3]$	58.5(58.8)	4.2(4.1)	6	16
$[HoCl_3(Ph_3PO)_3]$	58.8(58.6)	4.3(4.1)	6	16
$[ErCl_3(Ph_3PO)_3]$	58.7(58.5)	3.9(4.1)	7	18
$[TmCl_3(Ph_3PO)_3]$	58.7(58.4)	4.0(4.1)	6	20
$[YbCl_3(Ph_3PO)_3]$	58.1(58.2)	4.1(4.1)	8	20
$[LuCl_3(Ph_3PO)_3]$	57.7(58.1)	3.8(4.1)	8	21
$[LaCl_2(Ph_3PO)_4]PF_6 \cdot H_2O$	57.8(58.2)	3.9(4.2)	15	
$[CeCl_2(Ph_3PO)_4]PF_6 \cdot H_2O$	57.5(58.1)	3.8(4.2)	16	
$[PrCl_2(Ph_3PO)_4]PF_6 \cdot H_2O$	58.5(58.1)	3.9(4.2)	16	
$[NdCl_2(Ph_3PO)_4]PF_6 \cdot H_2O$	57.1(58.0)	3.8(4.2)	16	
$[SmCl_2(Ph_3PO)_4]PF_6$	57.8(58.5)	3.3(4.0)	17	
$[EuCl_2(Ph_3PO)_4]PF_6$	57.8(58.4)	3.9(4.1)	17	
$[GdCl_2(Ph_3PO)_4]PF_6$	57.6(58.2)	3.8(4.1)	16	
$[TbCl_2(Ph_3PO)_4]PF_6$	57.6(58.1)	3.8(4.0)	17	
$[DyCl_2(Ph_3PO)_4]PF_6$	58.3(58.0)	3.9(4.1)	17	
$[HoCl_2(Ph_3PO)_4]PF_6$	57.7(57.9)	3.7(4.0)	17	
$[ErCl_2(Ph_3PO)_4]PF_6$	57.8(57.8)	3.5(4.0)	17	
$[TmCl_2(Ph_3PO)_4]PF_6$	57.2(57.7)	3.7(4.0)	17	
$[YbCl_2(Ph_3PO)_4]PF_6$	57.2(57.6)	3.9(4.0)	16	
$[LuCl_2(Ph_3PO)_4]PF_6$	57.2(57.5)	3.9(4.0)	18	
$[LaCl_2(Ph_3PO)_4]Cl \cdot 2H_2O$ [e]	61.6(62.0)	4.5(4.6)	3	6
$[CeCl_2(Ph_3PO)_4]Cl \cdot 2H_2O$	62.0(62.0)	4.5(4.6)	3	6
$[PrCl_2(Ph_3PO)_4]Cl \cdot 2H_2O$	62.2(61.9)	4.6(4.6)	3	8
$[NdCl_2(Ph_3PO)_4]Cl \cdot 2H_2O$	61.9(61.8)	4.5(4.6)	3	8
$[SmCl_2(Ph_3PO)_4]Cl \cdot 2H_2O$	61.3(61.5)	4.1(4.6)	4	7
$[EuCl_2(Ph_3PO)_4]Cl \cdot 2H_2O$	61.8(61.4)	4.7(4.5)	5	9
$[GdCl_2(Ph_3PO)_4]Cl \cdot 2H_2O$	61.5(61.2)	4.1(4.6)	7	15
$[TbCl_2(Ph_3PO)_4]Cl \cdot 2H_2O$	61.3(61.1)	4.5(4.5)	7	16
$[DyCl_2(Ph_3PO)_4]Cl \cdot 2H_2O$	61.1(61.0)	4.2(4.5)	8	17
$[HoCl_2(Ph_3PO)_4]Cl \cdot 2H_2O$	61.2(60.8)	4.4(4.5)	8	19
$[ErCl_2(Ph_3PO)_4]Cl \cdot 2H_2O$	60.8(60.8)	4.6(4.6)	8	20
$[TmCl_2(Ph_3PO)_4]Cl \cdot 2H_2O$	60.4(60.6)	4.4(4.5)	10	20
$[YbCl_2(Ph_3PO)_4]Cl \cdot 2H_2O$	60.3(60.5)	4.4(4.5)	14	22
$[LuCl_2(Ph_3PO)_4]Cl \cdot 2H_2O$	60.2(60.5)	4.5(4.5)	15	23

[a] Calculated values in parenthesis.

[b] 10^{-3} mol dm^{-3} CH_2Cl_2 solutions.

[c] Freshly prepared 10^{-3} mol dm^{-3} solution.

[d] Solution in footnote c containing approximately 3 equivalents of Ph_3PO.

[e] Calculated data refer to dihydrates but in most samples ^{1}H NMR spectra show a mixture of water and ethanol present (see discussion in text). The effect on the analyses is small due to the large molecular weights of the cations.

2.2. *$[LnCl_3(Ph_3PO)_3]$*

These complexes are best obtained by reaction of $LnCl_3 \cdot nH_2O$ with Ph_3PO in a 1:3.5 molar ratio in hot acetone, and providing the solutions are not too concentrated on mixing, materials of adequate analytical purity separate directly from the solutions. The complexes are poorly soluble in acetone or alcohols, and more soluble in chlorocarbons. In 10^{-3} mol dm^{-3} CH_2Cl_2 solutions they have small conductivities which increase along the series (Table 1) but at 1–8 Ω^{-1} cm^2 mol^{-1}, are interpreted as non-conductors, the NMR studies (below) providing an explanation for the observed values. The conductances rise on addition of excess Ph_3PO, those of complexes in the latter half of the series progressively approaching 1:1 electrolytes. The IR

Table 2
Spectroscopic data

Complex	ν(PO) (cm^{-1a})	ν(Ln–Cl) (cm^{-1a})	$\delta(^{31}P)^b$
$[LaCl_3(Ph_3PO)_3]$	1147, 1171	220	35.8(10)
$[CeCl_3(Ph_3PO)_3]$	1146, 1172	225	78(1650)
$[PrCl_3(Ph_3PO)_3]$	1145, 1175	225, 237sh	130(700)
$[NdCl_3(Ph_3PO)_3]$	1147, 1176	228, 235sh	136(500)
$[SmCl_3(Ph_3PO)_3]$	1150, 1176	229	29(150)
$[EuCl_3(Ph_3PO)_3]$	1150, 1184	231	−70(600)
$[GdCl_3(Ph_3PO)_3]$	1152, 1186	230	n.o.
$[TbCl_3(Ph_3PO)_3]$	1153, 1184	228	−95(800), −129*
$[DyCl_3(Ph_3PO)_3]$	1154, 1188,	228	n.o., 17*
$[HoCl_3(Ph_3PO)_3]$	1153, 1188	229	49(1800), −6*
$[ErCl_3(Ph_3PO)_3]$	1154, 1188	239	−91(650), −87*
$[TmCl_3(Ph_3PO)_3]$	1155, 1189	236	−38(530), −20*
$[YbCl_3(Ph_3PO)_3]$	1155, 1187	240	21(650), 33*
$[LuCl_3(Ph_3PO)_3]$	1156, 1190	240	36.0(10), 37.2*
$[LaCl_2(Ph_3PO)_4]PF_6 \cdot H_2O$	1139	226	37.8(8)
$[CeCl_2(Ph_3PO)_4]PF_6 \cdot H_2O$	1141	235	80(100)
$[PrCl_2(Ph_3PO)_4]PF_6 \cdot H_2O$	1140	237	131(130)
$[NdCl_2(Ph_3PO)_4]PF_6 \cdot H_2O$	1142	237	138(90)
$[SmCl_2(Ph_3PO)_4]PF_6$	1142	236	30 (100)
$[EuCl_2(Ph_3PO)_4]PF_6$	1143	235	−75(400)
$[GdCl_2(Ph_3PO)_4]PF_6$	1145	237	n.o.
$[TbCl_2(Ph_3PO)_4]PF_6$	1146	238	−130(450)
$[DyCl_2(Ph_3PO)_4]PF_6$	1146	238	17(860)
$[HoCl_2(Ph_3PO)_4]PF_6$	1148	241	−6 (870)
$[ErCl_2(Ph_3PO)_4]PF_6$	1148	240	−87(340)
$[TmCl_2(Ph_3PO)_4]PF_6$	1149	240	−20(100)
$[YbCl_2(Ph_3PO)_4]PF_6$	1150	241	33(80)
$[LuCl_2(Ph_3PO)_4]PF_6$	1150	240	37.3(10)
$[LaCl_2(Ph_3PO)_4]Cl \cdot 2H_2O^c$	1140	224	33.5(br), see text
$[CeCl_2(Ph_3PO)_4]Cl \cdot 2H_2O$	1141	237	80(120), 78**
$[PrCl_2(Ph_3PO)_4]Cl \cdot 2H_2O$	1141	237	131(sh), 129**
$[NdCl_2(Ph_3PO)_4]Cl \cdot 2H_2O$	1141	240	138(100), 136sh**
$[SmCl_2(Ph_3PO)_4]Cl \cdot 2H_2O$	1143	229	30(110), 29**
$[EuCl_2(Ph_3PO)_4]Cl \cdot 2H_2O$	1144	236	−74(450), −70**
$[GdCl_2(Ph_3PO)_4]Cl \cdot 2H_2O$	1145	238	n.o.
$[TbCl_2(Ph_3PO)_4]Cl \cdot 2H_2O$	1146	240	−130(500), −94**
$[DyCl_2(Ph_3PO)_4]Cl \cdot 2H_2O$	1146	239	17(900), n.o.**
$[HoCl_2(Ph_3PO)_4]Cl \cdot 2H_2O$	1147	238	−6(550), 49**
$[ErCl_2(Ph_3PO)_4]Cl \cdot 2H_2O$	1147	239	-87(360), −91**
$[TmCl_2(Ph_3PO)_4]Cl \cdot 2H_2O$	1150	240	-20(110), −38**
$[YbCl_2(Ph_3PO)_4]Cl \cdot 2H_2O$	1150	240	33(90), 21**
$[LuCl_2(Ph_3PO)_4]Cl \cdot 2H_2O$	1150	242	38.0(15), 36.5**

[a] Nujol mulls.

[b] CH_2Cl_2 solution at 295 K relative to external H_3PO_4. The values in parenthesis are approximate line widths at half height ($W^{1/2}$ (Hz)). n.o. – not observed. Resonances marked * are due to $[LnCl_2(Ph_3PO)_4]^+$ formed in solution by rearrangement (see text), resonances marked ** are similarly due to $[LnCl_3(Ph_3PO)_3]$ and all the latter are accompanied by free Ph_3PO (not listed).

[c] See footnote e in Table 1.

spectra show broad and sometimes asymmetric υ(PO) modes in the range 1145–1156 cm^{-1} with a shoulder at 1170–1190 cm^{-1}, the major feature(s) slightly higher for each specific Ln than observed in the corresponding $[LnCl_2(Ph_3PO)_4]^+$, and broad weak bands in the range 220–240 cm^{-1} are assigned as ν(Ln–Cl). In neither case is there sufficient resolved splitting of ν(PO) or ν(Ln–Cl) to clearly distinguish *mer* (three IR active modes) from *fac* (two IR active modes) isomers. In a number of cases crystals of the complexes separated on standing from the synthesis solutions, but as observed in related systems [3–6,12] despite good visual appearance these often gave rather mediocre quality X-ray structural data, possible causes including fractional occupancies by solvent molecules and some disorder in the ligand phenyl rings. However, crystal structures were obtained for $[LnCl_3(Ph_3PO)_3] \cdot 0.5Me_2CO$ (Ln = La and Ce). Both were found to be 6-coordinate and meridional geometrical isomers, and the structures are isomorphous, although of low quality. Both the Ln residues in the cell had the same stereochemistry but during the refinement it became clear that there were disorder problems with a few of the phenyl rings (out of the 18) and the final R_1 values were 0.12(Ce) [2] and 0.13(La). [3] The key points are the Cl–Ln–Cl (Ce: 91.9(1), 92.7(1), 174.7(1)°. La: 91.9(2), 92.9(2), 174.2(2)°) and the O–Ln–O (Ce: 86.1(3), 91.1(3), 176.9(3)°. La: 85.3(5), 91.8(4), 177.0(4)°) which establishes the *mer* isomer. As in the tetrakis species (see later) the Ln–O–P angles are large (Ce: 164.5(6)–178.5(6)°. La: 165.1(8)–177.7(9)°).

The ^1H NMR spectra are uninformative but the $^{31}P\{^1H\}$ NMR (Table 2) are more useful, except for $[GdCl_3(Ph_3PO)_3]$ for which no resonance was observed, and $[DyCl_3(Ph_3PO)_3]$ which showed only a weak resonance assigned to $[DyCl_2(Ph_3PO)_4]^+$ the absence of the expected resonances being attributable to fast relaxation. For the complexes of Tb–Lu, two resonances were present (Table 2) the narrower one of which could be identified as due to $[LnCl_2(Ph_3PO)_4]^+$ by comparison with the spectra obtained from $[LnCl_2(Ph_3PO)_4]PF_6$ and the second broader signal is assigned to $[LnCl_3(Ph_3PO)_3]$. The mass balance requires at least one other lanthanide species to be formed, and since no other ^{31}P NMR resonances are seen, this is presumably phosphine oxide free. Possible equilibria would include:

$$4[LnCl_3(Ph_3PO)_3] \leftrightarrow 3[LnCl_2(Ph_3PO)_4]^+ + [LnCl_x]^{(x-3)-} + (6-x)Cl^-.$$

In an attempt to probe this equilibrium, ^{139}La NMR spectra were recorded from solutions of $[LaCl_3(Ph_3PO)_3]$ in CH_2Cl_2 and MeCN. The ^{139}La nucleus ($I = 7/2$, 99.9%, $\Xi = 14.1$ MHz, quadrupole moment 0.20×10^{-28} m^2) is not particularly suited to such studies, the combination of the substantial quadrupole and the lability of many complexes often resulting in lines too broad to observe. Most of the species for which a resonance has been observed are of high symmetry usually LaL_6 type [17]. We reported the chemical shift of $[La(Me_3PO)_6]^{3+}$ as +116 [13] and those of other LaO_6 moieties lie in the region ca. 0–200 ppm [17]. In previous studies [5] of the $[La(NO_3)_3(Ph_3PO)_x]$ systems we did not observe any lanthanum resonances, clearly due to the line-broadening caused by fast quadrupolar relaxation in the low symmetry environments, and similarly resonances are not expected for $[LaCl_3(Ph_3PO)_x]$. However both CH_2Cl_2 and MeCN solutions of $[LaCl_3(Ph_3PO)_3]$ showed a broad resonance at ca. δ 600 ($W_{1/2} = 3000$ Hz), which is in poor agreement with that reported for $[LaCl_6]^{3-}$ in MeCN δ 851 [18]. The resonance is largely lost on adding excess Ph_3PO to the solution, suggesting it is a lanthanum chlorospecies which is consumed as the equilibrium shifts.

Addition of Ph_3PO to these $[LnCl_3(Ph_3PO)_3]$ solutions changed the relative intensities of the resonances in favour of that of the tetrakis complex, confirming their assignments and the presence of a free Ph_3PO resonance in the majority of examples showed exchange was slow on the NMR time scale. The relative amount of the tetrakis complex present increases along the series which explains the increasing conductances of their solutions. For the early members of the series Ce–Nd only a single $^{31}P\{^1H\}$ NMR resonance of coordinated phosphine oxide was observed. For these elements the very similar chemical shifts of the tris and tetrakis species (Table 2) makes it very difficult to identify small amounts of one in the presence of the other, but from the very small conductances it seems probably that rearrangement into the tetrakis complexes is minimal here. The diamagnetic $[LaCl_3(Ph_3PO)_3]$ shows only a single sharp ($W_{1/2} = 10$ Hz) resonance which was unexpected given the structure of the solid (above) reveals a *mer* arrangement of Ph_3PO groups. It is not possible from the available data to distinguish between complete rearrangement into the *fac* form, fluxionality or accidental coincidence of the resonances. The last seems most likely, since although the nitrate systems are usually fluxional [4–6] these are mostly 9-coordinate, and fluxionality is less likely in 6-coordination. In contrast to the other complexes, addition of Ph_3PO to a solution of $[LaCl_3(Ph_3PO)_3]$ in CH_2Cl_2 showed only a broad singlet indicative of fast exchange, and cooling the solution below 243 K was necessary to resolve separate resonances. At 195 K resonances attributable to $[LaCl_3(Ph_3PO)_3]$, $[LaCl_2(Ph_3PO)_4]^+$, Ph_3PO and a new unidentified species with δ 33 were present. Since lanthanum is the largest of the lanthanides, it is not possible to rule out that this unassigned species may be the 7-coordinate $[LaCl_3(Ph_3PO)_4]$, although it could also be the second geometric isomer of $[LaCl_3(Ph_3PO)_3]$.

2.3. $[LnCl_2(Ph_3PO)_4]Cl \cdot n(solv)$ (solv = H_2O or EtOH)

These complexes were obtained from hot ethanol solutions of $LnCl_3 \cdot nH_2O$ and 6 mol. equivalents of Ph_3PO, and were always obtained solvated (see above). As expected the IR spectra were very similar to those of

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[2] $[CeCl_3(Ph_3PO)_3] \cdot 0.5Me_2CO$. Crystals were isolated from the preparation. Crystal data: monoclinic; $a = 19.529(5)$; $b = 15.5490(10)$; $c = 34.844(4)$ Å; $\beta = 103.738(3)°$, $V = 10277.9(17)$ Å^3. $Z = 8$, RMM = 1110.32, $T = 120$ K. Data collected on a Nonius Kappa CCD diffractometer using Mo Kα radiation. Space group $P2_1/n$ (no. 14) from systematic absences. The data were rather weak ($\langle I/\sigma(I)\rangle = 3.5$) with $R_{int} = 0.11$, and although the two mer octahedral species in the asymmetric unit were clearly established (Ce–Cl 2.696(4)–2.755(4) Å; Ce–O 2.344(9)–2.421(11) Å) there was disorder in the phenyl rings and refinement failed to reduce R_1 ($I > 2\sigma(I)$) below 0.12.

[3] $[LaCl_3(Ph_3PO)_3] \cdot 0.5Me_2CO$. Crystals were isolated from the preparation. Crystal data: monoclinic; $a = 19.574(5)$; $b = 15.608(4)$; $c = 34.837(8)$ Å; $\beta = 103.890(8)°$, $V = 10332(4)$ Å^3. $Z = 8$, RMM = 1109.11, $T = 120$ K. Data collected on a Nonius Kappa CCD diffractometer using Mo Kα radiation. Space group $P2_1/n$ (no. 14) from systematic absences. The data were rather weak ($\langle I/\sigma(I)\rangle = 5.0$) with $R_{int} = 0.08$, and although the two mer octahedral species in the asymmetric unit were clearly established (La–Cl 2.712(7)–2.776(5) Å; La–O 2.351(14)–2.451(14) Å) there was disorder in the phenyl rings and refinement failed to reduce R_1 ($I > 2\sigma(I)$) below 0.13.

$[LnCl_2(Ph_3PO)_4]PF_6$, except for the absence of the $[PF_6]^-$ and the presence of solvate molecule vibrations. The presence of *trans* pseudooctahedral cations was confirmed in two cases by X-ray studies on the Tb and Yb compounds. The crystal structures (see Tables 3 and 4 and Fig. 1) are essentially isomorphous with only small differences in the anion disorder and extent of solvation being observed. The cations have no crystallographic symmetry but in both cases the two Ln–Cl distances are similar as are the Ln–O distances. As expected the Yb distances are on average shorter than the Tb distances by approximately 0.05 Å. All the bond angles at Ln are within 6° of the ideallised value of 90°. The geometry of the triphenylphosphine oxide ligand is unexceptional and the Ln–O–P angle which is very variable in phosphine oxide complexes is large, spanning the range 167–177°. Disordered EtOH molecules were clearly identified in both structures but it proved difficult to convincingly associate residual peaks in the electron density maps with $O(H_2)$ molecules.

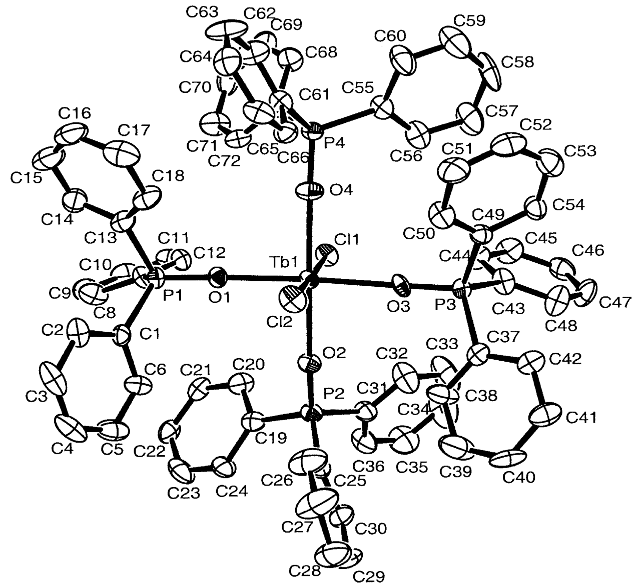

Fig. 1. The structure of the cation in $[TbCl_2(Ph_3PO)_4]Cl \cdot 1.55EtOH$ showing the atom labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and the H atoms are omitted for clarity. The structure of the Yb cation is very similar and the same numbering scheme has been adopted

In contrast to the data on the $[LnCl_2(Ph_3PO)_4]PF_6$ salts, the $^{31}P\{^1H\}$ NMR spectra from CH_2Cl_2 solutions (Table 2) mostly show three species identified as $[LnCl_2(Ph_3PO)_4]^+$, $[LnCl_3(Ph_3PO)_3]$, and Ph_3PO present. For $[LaCl_2(Ph_3PO)_4]Cl$ only a broad resonance at δ 34 was present, but on cooling to 200 K this resolved into resonances at 36 ($[LaCl_3(Ph_3PO)_3]$), a very weak shoulder at 37.5 ($[LaCl_2(Ph_3PO)_4]^+$), Ph_3PO, and an unassigned species with δ 33. This data and the very small conductance of the solution (Table 1) shows that

Table 3
Selected bond lengths (Å) and angles (°) for $[TbCl_2(Ph_3PO)_4]Cl \cdot 1.55EtOH$

Tb(1)–Cl(1)	2.633(3)	Tb(1)–Cl(2)	2.647(2)
Tb(1)–O(1)	2.260(6)	Tb(1)–O(3)	2.252(6)
Tb(1)–O(2)	2.269(6)	Tb(1)–O(4)	2.266(7)
P–O	1.496(7)–1.519(7)	P–C	1.788(10)–1.820(10)
Cl(1)–Tb(1)–Cl(2)	176.23(8)	O(2)–Tb(1)–O(3)	88.2(2)
O(1)–Tb(1)–O(2)	88.8(2)	O(2)–Tb(1)–O(4)	173.3(2)
O(1)–Tb(1)–O(3)	176.8(2)	O(3)–Tb(1)–O(4)	92.1(2)
O(1)–Tb(1)–O(4)	91.0(2)		
Cl(1)–Tb(1)–O	86.2(2)–91.8(2)	Cl(2)–Tb(1)–O	89.3(2)–96.3(2)
Tb(1)–O(1)–P(1)	177.5(4)	Tb(1)–O(3)–P(3)	171.3(4)
Tb(1)–O(2)–P(2)	167.2(4)	Tb(1)–O(4)–P(4)	170.6(4)
O–P–C	108.5(4)–112.7(4)	C–P–C	105.1(5)–109.9(4)

Table 4
Selected bond lengths (Å) and angles (°) for $[YbCl_2(Ph_3PO)_4]Cl \cdot 2.25EtOH$

Yb(1)–Cl(1)	2.590(3)	Yb(1)–Cl(2)	2.585(2)
Yb(1)–O(1)	2.205(8)	Yb(1)–O(3)	2.188(8)
Yb(1)–O(2)	2.216(8)	Yb(1)–O(4)	2.217(8)
P–O	1.488(8)–1.512(8)	P–C	1.777(13)–1.826(14)
Cl(1)–Yb(1)–Cl(2)	177.15(10)	O(2)–Yb(1)–O(3)	90.2(3)
O(1)–Yb(1)–O(2)	91.9(3)	O(2)–Yb(1)–O(4)	173.8(3)
O(1)–Yb(1)–O(3)	177.6(3)	O(3)–Yb(1)–O(4)	89.8(3)
O(1)–Yb(1)–O(4)	88.2(3)		
Cl(1)–Yb(1)–O	86.6(2)–91.7(2)	Cl(2)–Yb(1)–O	89.3(2)–95.5(2)
Yb(1)–O(1)–P(1)	171.0(5)	Yb(1)–O(3)–P(3)	175.1(5)
Yb(1)–O(2)–P(2)	170.4(5)	Yb(1)–O(4)–P(4)	167.4(5)
O–P–C	108.5(5)–113.7(6)	C–P–C	105.9(6)–109.5(7)

decomposition to form $[LaCl_3(Ph_3PO)_3]$ is close to complete. For the succeeding elements Ce–Sm, the solution conductances are also low and the $^{31}P\{^1H\}$ NMR spectra show a strong Ph_3PO resonance and broad features due to the coordinated phosphine oxide, consistent with extensive dissociation into the neutral tris complex. For Eu–Tm the conductances rise steadily and for these complexes the $^{31}P\{^1H\}$ NMR spectra clearly show both tris and tetrakis complexes (and free Ph_3PO) present, whilst for Yb and Lu the data supports the tetrakis species as the major solution form, although even here the spectra still show some $[LnCl_3(Ph_3PO)_3]$ present. In earlier studies these low conductances were interpreted as evidence for neutral 7-coordinate $[LnCl_3(Ph_3PO)_4]$ complexes in solution, but with the NMR data available, it is now clear that the mixed solution speciation is responsible for the low values and the complexes are based upon 6-coordinate cations.

3. Summary and conclusions

The studies have shown that $[LnCl_3(Ph_3PO)_3]$ and $[LnCl_2(Ph_3PO)_4]^+$ co-exist in solutions of lanthanide chlorides – Ph_3PO in weakly coordinating solvents. Pure samples of either can be isolated by choice of appropriate conditions, and in solution the equilibria are readily shifted by addition of Cl^- or Ph_3PO, but there was no evidence for the formation of species with fewer than three or more than four-coordinated phosphine oxides, although complexes of the latter type, $[LnCl(Ph_3PO)_5]^{2+}$ can be isolated by chloride abstraction using strong Lewis acids [8]. There is a clear trend along the lanthanide series with $[LnCl_3(Ph_3PO)_3]$ strongly favoured at the beginning of the series and $[LnCl_2(Ph_3PO)_4]^+$ towards the end. A question arises about how the solvents affect the speciation – does the isolation of $[LnCl_3(Ph_3PO)_3]$ from acetone mean these are the major solution species in this solvent? It appears not. Taking Tm as an example, since it shows sharp well separated $^{31}P\{^1H\}$ NMR resonances for each species making for easy identification, acetone solutions of either $[TmCl_3(Ph_3PO)_3]$ or $[TmCl_2(Ph_3PO)_4]^+$ show both species present. However, $[TmCl_3(Ph_3PO)_3]$ is only slightly soluble in cold acetone, and this poor solubility rather than essentially different solution speciation probably accounts for its ready isolation from acetone solution, the fast solution equilibria permitting crystallisation of the least soluble form. Similarly both species are present in MeCN solution, and probably in EtOH, although in ethanol there are moderate solvent shifts (<3 ppm) on the major resonances and it may be that some ethanol coordination occurs. We have not however isolated any complexes of the type $[LnCl_3(Ph_3PO)_2(EtOH)]$ in this work, although $[Ln(NO_3)_3(Ph_3PO)_2(EtOH)]$ are well established in the nitrate systems [2,4]. The data suggest that $[LnCl_2(Ph_3PO)_4]Cl$ are only the major solution species for the last few elements of the series, and their isolation in the solid state for the others depends upon slow crystallisation from solutions containing excess phosphine oxide.

4. Experimental

Hydrated lanthanide chlorides were obtained commercially (BDH, Aldrich or Alfa) or made by reaction of the corresponding oxides with aqueous hydrochloric acid. Absolute ethanol (Aldrich) and other solvents were used as received. $^{31}P\{^1H\}$ NMR spectra were obtained on a Bruker DPX400 at 161.9 MHz and are referenced to external 85% H_3PO_4, and ^{139}La spectra similarly at 56.6 MHz and referenced to $[La(H_2O)_x]^{3+}$ at pH 1 in water. Other physical measurements were made as described [5,12,13].

The complexes were made by a number of general methods, representative examples of which are described. Whilst the $[PF_6]^-$ salts are readily obtained, isolation of pure samples of the tris or tetrakis chloro-complexes was best achieved under conditions where they separated slowly from solution. Use of concentrated solutions from which immediate precipitation occurred on mixing rarely yielded pure samples, and since recrystallisation often fails to improve purity due to the equilibria present as discussed above, isolation of pure samples from the reaction mixtures is preferable. Analytical data and selected spectroscopic data are given in Tables 1 and 2.

4.1. $[La(Ph_3PO)_3Cl_3]$

A solution of $LaCl_3 \cdot 7H_2O$ (0.425 g, 1.1 mmol) in acetone (5 cm^3) was added to a solution of Ph_3PO (1.11 g, 4.0 mmol) in acetone (10 cm^3) and the mixture refluxed for 20 min. The solution was then cooled and refrigerated for 24 h. The white powder was filtered off and dried in vacuo. Yield: 0.45 g (38%). ^1H NMR ($CDCl_3$) 300 K. 7.35–7.70(m).

4.2. $[PrCl_2(Ph_3PO)_4]Cl \cdot n(solv)$

A solution of $PrCl_3 \cdot 7H_2O$ (0.38 g, 1.0 mmol) in boiling absolute ethanol (10 cm^3) was added to a solution of Ph_3PO (1.67 g, 6.0 mmol) in hot ethanol (15 cm^3) and the mixture refluxed for 20 min. It was allowed to cool to room temperature, filtered to remove any solid, and the filtrate refrigerated for 24 h. Very pale greenish crystals separated, which were filtered off, rinsed with diethyl ether (10 cm^3) and dried in vacuo. Yield: 0.60 g (43%).

4.3. $[CeCl_2(Ph_3PO)_4]PF_6 \cdot H_2O$

Solutions of $CeCl_3 \cdot 7H_2O$ (0.18 g, 0.50 mmol) in ethanol (10 cm^3) and $[NH_4][PF_6]$ (0.082 g, 0.50 mmol) in ethanol (10 cm^3) were mixed and stirred for 5 min. A solution of Ph_3PO (0.56 g, 2.0 mmol) in ethanol (10 cm^3) was added resulting in an immediate precipitate. The mixture was stirred for 1 h and left to stand overnight. The precipitate was then filtered off, rinsed with cold ethanol (5 cm^3) and dried in vacuo. Yield: 0.46 g (62%).

4.4. Crystal structure determinations

Suitable crystals were isolated from the syntheses in ethanol solution and attempts to grow crystals using the solid products were not successful. Data were recorded at 120 K using a Nonius CCD diffractometer fitted with graphite-monochromator and Mo Kα radiation. An empirical absorption correction using the SORTAV procedure [19] was applied and the crystallographic data are given in Table 5. The structures were solved in space group $P2_1/c$ using direct methods [20] to locate the heavy atoms (Ln, Cl, P and O) and subsequent structure-factor and electron-density calculations located the remaining non-hydrogen atoms. H atoms on the phenyl groups were added in calculated positions and full-matrix least-squares refinement on F^2 [21] was carried out to convergence. While the cation structure was well behaved both the structures had disordered atoms associated primarily with the ethanol solvate molecules. For the Tb structure rather surprisingly there was disorder in the Cl^- anion with one position being shared by an EtOH molecule. The site occupation factor (sof) was reduced for the remaining EtOH molecules in both the Tb and Yb structures to reduce the large isotropic atomic displacement parameters values of the C and O atoms to more normal values. The rather large residual electron-density peaks were close to EtOH molecules and represent inadequately modelled disorder and may even be $O(H_2)$ molecules as noted in the NMR spectra.

5. Supplementary material

Atomic coordinates, atomic displacement parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC) as CCDC Nos. 211998 (Tb) and 211999 (Yb). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Table 5
Crystallographic data for $[MCl_2(Ph_3PO)_4]Cl \cdot n$EtOH (M = Tb and Yb)[a]

Compound	$[TbCl_2(Ph_3PO)_4]Cl \cdot 1.55EtOH$	$[YbCl_2(Ph_3PO)_4]Cl \cdot 2.25EtOH$
Empirical formula	$C_{75.10}H_{69.30}Cl_3O_{5.55}P_4Tb$	$C_{76.50}H_{73.50}Cl_3O_{6.25}P_4Yb$
Formula weight	1449.76	1496.12
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)
a (Å)	14.563(2)	14.431(3)
b (Å)	17.364(2)	17.456(4)
c (Å)	29.571(4)	29.261(7)
β (°)	97.238(5)	97.563(10)
U (Å^3)	7417.9(13)	7307(3)
D_{calc} (g cm^{-3})	1.298	1.360
Z	4	4
$F(000)$	2961	3054
Crystal size (mm)	0.16 × 0.16 × 0.12	0.16 × 0.12 × 0.10
Reflections measured	57950	36126
Unique reflections (R_{int})	12885 (0.11)	11939 (0.13)
hkl range	−13 to 17, −20 to 20, −35 to 35	−15 to 17, −20 to 19, −33 to 34
Maximum, minimum transmission	1.005, 0.948	0.970, 0.942
Data in refinement	12885	11939
Parameters	786	793
μ (cm^{-1})	11.95	15.27
S	1.025	1.040
Maximum shift/esd	0.004	0.002
Residual electron density (eÅ^{-3})	−1.16 to +3.04	−1.16 to +3.10
$R^b(I > 2\sigma(I))$	0. 082 (8496 reflections)	0.089 (6581 reflections)
R (all data)	0.131	0.173
$wR_2{}^c$(all data)	0.248	0.241

[a] In common: λ(Mo Kα) = 0.71073 Å; T = 120 K; max. $2\theta = 50.0°$; SORTAV absorption correction [19].
[b] $R = \sum ||F_o| - |F_c|/\sum |F_o|$.
[c] $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$.

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